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1,4-DIPHENYLBUTADIYNE AS A POTENTIAL TRITIUM GETTER

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ABSTRACT

Research on the acetylene compound 1,4-diphenylbutadiyne is an effort to develop a tritium gas getter that will operate in the presence of air and minimize the formation of water. T_2 adds to the acetylene bond of the getter in the presence of a metal catalyst. The catalyst stimulates the T_2 - O_2 reaction as well. The butadiyne compound has shown good reaction efficiency for 300 ppm T_2 in static dry air at room temperature and one atmosphere pressure. Metal-acetylene complexes are being synthesized, positioning the metal catalyst atom as close to the triple bond as possible to maximize the organic reaction. Organometallics such as triphenylphosphine iridium are being investigated as possible regenerative getters for T_2 in air. Gas mixtures as low as 1 ppm T_2 in air will be tested under flow conditions in future work.

CURRENT TECHNOLOGY

At a fusion reactor there is a possibility of a tritium release into the air of a room. There is no substance used presently that will directly react with tritium in the presence of air. Instead, T_2 is reacted with oxygen over a palladium catalyst to form tritiated water, which is then adsorbed on a zeolite bed. Since tritiated water is a far more toxic form of tritium than tritium gas, we have undertaken the study of compounds that will react directly with tritium in the presence of air. We have concentrated on the hydrogenation of acetylene.

The first organic getter was studied at Sandia, Albuquerque.¹⁻³ The getter was intended for hydrogen in atmospheres not containing oxygen. The researchers selected DPPE (dimerized phenylpropargyl ether), $C_{18}H_{14}O_2$, [2,4-hexadiyne; 1,6-diol, 1,6-diphenyl-] which possesses two carbon-carbon triple bonds. The H_2 reacted efficiently at room temperature in the presence of

palladium catalyst on calcium carbonate. There was some evidence of reaction in air, however no catalyst blank was run for comparison.¹ The compound reacted incompletely with pure tritium then outgassed due to possible radiation damage.³

We select 1,4-Diphenylbutadiyne,⁴ $C_{16}H_{10}$, 87°C, [benzene; 1,1'-(1,3-butadiyne-1,4-diyl)bis-], which is a hydrocarbon of the structure $C_6H_5-C\equiv C-C\equiv C-C_6H_5$. As is the case with the Sandia compound, the phenyl groups are present to add radiation stability. The ether linkages on the Sandia compound have been replaced with carbon-carbon bonds to further improve stability. Mike Smith, of Bendix, has determined that DPPE's ether linkages are subject to breakage during conventional hydrogenation and selected the hydrocarbon as an improved hydrogen getter.⁵

EXPERIMENTAL RESULTS

1,4-Diphenylbutadiyne was evaluated at room temperature and 1 atmosphere pressure at tritium concentrations ranging from 300-500ppm T_2 in static dry air. Substrates used to support the organic and catalyst include calcium carbonate, carbon, chromosorb w, fluoropak 80 (a nylon) and firebrick. Two experiments of 300ppm T_2 in argon were completed to measure the extent of water formation in inert atmosphere. The data on 1,4-diphenylbutadiyne with palladium catalyst on calcium carbonate showed the reaction to be dominated by the formation of HTO with only 11% of the input tritium going on the organic getter. Examination of this material by electron microscopy (SEM) and x-ray photoelectron spectroscopy (ESCA) revealed that the organic layer was distributed unevenly over the palladium/calcium carbonate (Fig. 1), producing localized areas of catalyst and substrate. The proximity of the metal catalyst to the triple bond of the organic is believed to be a critical parameter in the gettering reaction. Since the catalyst works on the oxygen as well as the tritium molecules to form free radicals, the farther the tritium radical must travel to react with the acetylene bond of the organic, the greater the probability that it will see an oxygen first and form hot water. This is amplified by the fact that oxygen atoms outnumber tritium atoms by three to four orders of magnitude. Therefore, considerable attention has been given to substrates and the technique of laying down the catalyst and organic.

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Our best results have been obtained from getter samples comprised of 20% (by weight) diphenylbutadiyne on firebrick substrate with 1% platinum metal. The tremendous surface area of this rigid honey-combed substrate allows for optimum coating by the organic and maximizes the number of available reaction sites, (Fig. 2). Among the experiments using 1% Pt, Run 54 stands out as exceptional; see Table 1. We observed 75% of the input tritium in the organic phase and only 5% in the aqueous phase. 18% was remaining in the substrate with no T₂ remaining unreacted in the gas phase.

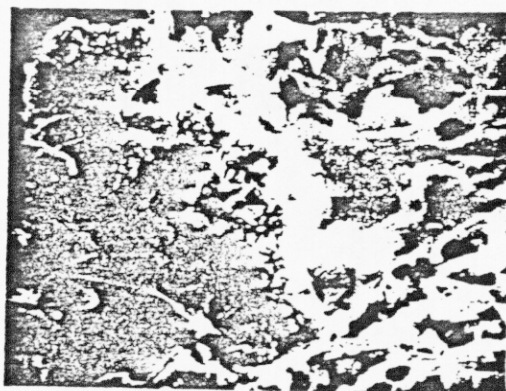


Fig. 1. 95%DPBD on Pd/CaCO₃ X3500

The material used in Runs 54 and 55 (20% 1,4-diphenylbutadiyne, 1% Pt on firebrick) was synthesized using aerosol-OT to change the surface characteristics of the substrate slightly and allow even coating of the platinum catalyst (K₂PtCl₄). The unique feature of the material used in Run 54 is that the reduction of the platinum metal using sodium borohydride was done in MIM (ethylene glycol monomethyl ether). In contrast, the identical material with the exception of being reduced in methanol showed only .6% of the input tritium in the organic phase, 60% in the aqueous phase and 23% in the substrate (Run 55). Run 42 used the same proportion of

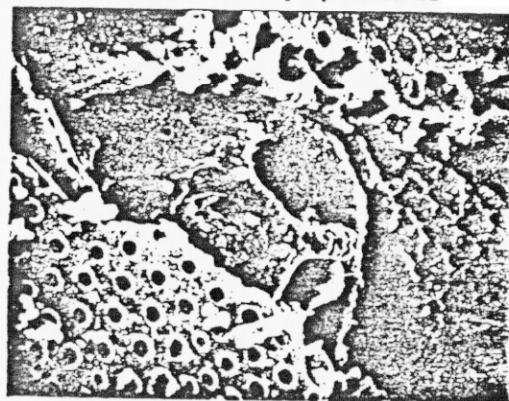


Fig. 2. 20%DPBD/1% Pt on Firebrick X3500

TABLE 1. GETTER RESULTS FOR 1,4-DIPHENYLBUTADIYNE AT 20°C and 1 ATM OF 300-500ppm T₂ IN STATIC AIR

RUN #	DPBD (w/w%)	SUBSTRATE	INITIAL MOLES			CATALYST (w/w%)	% T IN PHASE			
			ORGANIC (e-3)	T ₂ (e-7)	O ₂ (e-4)		ORGANIC	WATER	SUBSTRATE	GAS
54	20	FIREBRICK	6	10	3	1% Pt	74.8	4.8	18.4	ND
55	20	FIREBRICK	6	9	2	1% Pt	0.6	59.5	23.4	ND
42	20	FIREBRICK	4	11	5	1% Pt	46.6	48.4	5.0	ND
30	20	FIREBRICK	5	6	5	1% Pd	32.6	64.3	—	NA
40	20	FIREBRICK	6	10	5	1% Pd	39.4	42.3	8.1	ND
52	20	FIREBRICK	6	12	4	1% Pd	19.9	31.5	8.3	ND
32	20	FIREBRICK	3	11	5	0.1% Pd	6.1	62.1	14.0	ND
51	80	FIREBRICK	7	11	2	1% Pd	19.7	15.6	3.3	ND
29	60	CaCO ₃	3	7	5	5% Pd	10.5	61.9	—	ND
35	60	CaCO ₃	3	9	None	5% Pd	10.6	22.4	—	NA ^a
43	20	FIREBRICK	6	12	4	1% Pd	19.5	45.6	3.0	ND
46	75	CARBON	7	12	5	~5% Pd	5.3	43.6	—	ND
34	20	Fluoropak 80	8	12	5	1% Pd	0.7	10.4	—	ND
33	20	Chromosorb W	8	12	5	1% Pd	6.5	49.7	—	ND
36	20	Chromosorb W	8	9	None	1% Pd	21.9	42.1	4.5	NA ^a
41	20	FIREBRICK	5	11	5	1% Ni	3.7	20.1	0.2	86.2
47	20	FIREBRICK	4	11	3	1% Au	2.4	11.4	0.4	59.3
48	20	FIREBRICK	3	13	3	.5% Au/.5% Pd	9.6	51.5	2.7	ND
38	20	FIREBRICK	6	11	6	0.2% Ir ^a	11.2	52.9	2.1	5.7 ^b
44	19.3	FIREBRICK	6	12	6	0.9% Ir ^a	6.8	7.5	0.3	59.4 ^c

^aVaska's Catalyst: Chlorocarbonylbis(Triphenylphosphine)Iridium

^aFeed Gas was T₂ in Argon

^bVaska's Catalyst: 45ppm HT + 170ppm H₂ remaining in gas phase (No UV activation, H₂ activation attempted)

^cVaska's Catalyst: No HT or H₂ remaining in gas phase (activation with UV)

ND - No detectable tritium remaining in gas phase

NA - No analysis of remaining gases

organic and catalyst but aerosol OT was not used in the synthesis; the catalyst was reduced in methanol as in Run 55. Here we found 46.6% of the tritium in the organic, 48.4% as water, 5% in the substrate and no T₂ remaining as gas. We observe that the use of aerosol-OT kills the reaction of tritium to the organic when methanol is used in the reduction of platinum but greatly enhances the organic reaction when the reduction is done in MIM. The remaining data in Table 1 ranges from a 50:50 split in the distribution of activity in the organic and aqueous phases for platinum on firebrick to a complete dominance of the water forming reaction for other catalysts and substrates. Runs 35 and 36 using 300ppm T₂ in argon showed 2:1 dominance of the water forming reaction over the organic. This probably was a result of exchange with trace quantities of water present in the substrate material despite the efforts to ensure dryness. A blank was run using only 1% palladium on firebrick in 500ppm T₂ in air. We found that 74% on the input T₂ had reacted to form water (HTO, T₂O) under these conditions.

DISCUSSION

Comparing the water and organic reactions we find that the thermodynamic values do not tell us much. The heat of formation of D₂O is -295 kJ/mole at 298°K with an equilibrium constant of K_{eq}=10⁴². The hydrogenation of aliphatic alkynes has a heat of reaction of about -140kJ/mole and an equilibrium constant of K_{eq}=10²³.⁶ Both reactions want to run to absolute completion.

To compare the reactions, rate data is needed. The catalyst provides an environment in which thermal energy is used to successfully pump up the evenly spaced molecular vibrational levels of H₂ and D₂ until dissociation occurs. The energies of dissociation for H₂ and O₂ are 436 and 498kJ/mole,⁷ meaning that atoms of both will be formed simultaneously. We may compare the following room temperature gas phase reactions, where the rate constants, k, are in cc/mole-sec:⁸⁻¹²



We see that the basic water forming reactions are not fast compared to the organic reaction. Ethene is known to be used as an inhibitor of the water reaction by reaction (4) above.¹³

What makes the formation of water so efficient is the reaction on or near the catalyst. The mechanism is unknown. It could start with



on the catalyst surface followed by reaction (2). Platinum quickly acquires a covering of oxygen atoms, so that reaction (3) is another possible mechanism.¹⁴ We conclude that there is no easy way to compare the rates of the water and organic reactions from first principles.

Two important points do emerge. The first is to try to keep O₂ away from the catalyst surface. To this end, the organic should surround the catalyst particle. The lighter mass T₂ will premeate the organic up to an order of magnitude faster than O₂; the principle used in membrane gas separation.¹⁵ The second point is that the distance between the catalyst and the organic should be as short as possible so that a tritium atom will meet few oxygen atoms or molecules while diffusing. The catalyst particles should be as small as possible. In the case of our Pt or Pd catalysts, this depends on minute details in the synthesis that are largely trial and error.

In an attempt to bring the metal atom closer to the triple bond we have made some preliminary investigation into organometallic catalysts. Vaska's catalyst, chlorocarbonylbis(triphenylphosphine)iridium(I), with the formula IrCl(CO)-(PPh₃)₂, where Ph indicates a phenyl group, is known to add H₂ (and O₂) directly to the metal atom with a weak bond.¹⁶⁻¹⁸ The H₂ can be regenerated when irradiated with ultraviolet light so that this class of compound could be an easy-regenerative getter.

Runs 38 and 44 were tests on the iridium complex in combination with 1,4-diphenylbutadiyne on firebrick. With no UV activation prior to T₂ exposure (Run 38), the iridium complex put only 11% of the tritium in the organic phase and 53% in the aqueous phase, leaving 6% T₂ unreacted. Quite different results were produced using UV activation, (Run 44), where 7% and 8% of the tritium was found in the organic and aqueous phases leaving 59% T₂ unreacted. It may be that the iridium had already reacted with the acetylene triple bond, thereby blocking out the T₂.¹⁹ In the case of no UV activation hydrogen was never purged from the metal thus preventing any T₂ addition there. The beta activity above was enough to initiate the water reaction.²⁰ The relatively small amount of hot water formed indicates that the iridium may have bonded oxygen when the mixture of 300ppm T₂ in dry air was added. We plan to evaluate the iridium complex as a getter without the presence of 1,4-diphenylbutadiyne to resolve some of this data.

FUTURE WORK

Our future work with getter systems will include optimizing the performance of the Pd/Pt getters as well as further investigation of organometallic complexes. It is apparent that bringing the metal atom and triple bond together in a single, fairly simple molecule will optimize the conditions for success. An example is (Ph C≡C Ph)₂ Pt,²¹ which has all the basic parts

is illustrated by our dielectric constant measurements at 1592 Hz and 2830 V/m. Liquid T_2 has 4×10^{10} electric charges/mole, of which 25 to 40% may be electrons. The ion yield is only about 10^{-3} ions pairs/100 e.v. The gas shows about 10^{12} static electric charges/mole, regardless of density. Less than 2% of the charges are probably electrons, and the ion yield is 0.15 - 0.5 ions pairs/100 ev.

It is clear that charge production is more efficient in the gas than in the liquid. In the gas, ions and electrons are further apart and less likely to recombine. In both cases, however, virtually all the current is carried by the high mobility electrons. The ions are about 2000 times slower. They register as static charges in the dielectric constant, but they have no appreciable effect on the electrical conductivity. Electrons may react to form tritide ions and possibly even larger species.²² This is why the percent of electrons is less than 50%.

Upon freezing, the solid pulls away from the walls and electrical contact is lost. Overpressures of 1 atm do not help. We are presently building a 200 atm electrical conductivity cell to attack this problem.

CONCLUSIONS

Our goal is to accumulate enough data on cryogenic D-T to allow fusion engineers to feel comfortable with this potential fuel. To this end, we are working on D_2 - T_2 chemical and rotational kinetics, solid thermal conductivity, and electrical properties.

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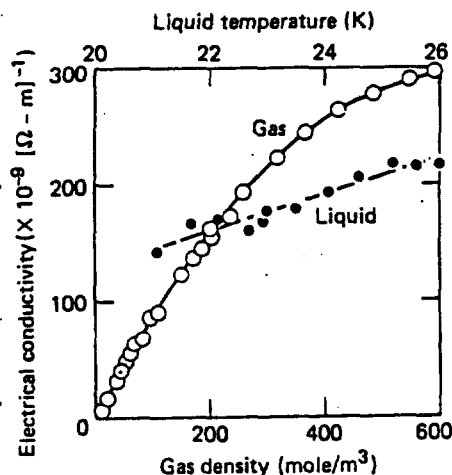


Fig. 5. Electrical conductivity of gaseous and liquid T_2 . Above 200 mole/m³, the gas is a better conductor.

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